TRANSLATION OF ANNEXES TO THE IPER

silane and a hydrolyzed multi-silyl-functional silane, but no fluorine-containing silane.

DE-A1-101 49 148 describes aqueous coating compositions based on organic film former, fine inorganic particles and also lubricants and/or organic corrosion inhibitor, the compositions providing outstanding results in corrosion resistance, adhesion and formability, not least on Galvalume® steel sheets, despite the absence of chromium compounds, but nevertheless also exhibiting inadequate corrosion resistance as an organic film approximately 1 µm thick on hot-dip-galvanized, electrolytically galvanized or Galfan®-coated metallic strips, i.e. on metallic surfaces which are difficult to protect against corrosion. The compositions, their constituents and the properties of the raw materials and coatings in that publication are expressly incorporated by reference into this specification.

The subject-matter of German Patent Application DE 103 08 237 of 25.02.2003, relating to compositions of similar constitution and to corresponding processes for coating metallic surfaces, is explicitly incorporated by reference in terms of the raw materials and their properties, the preparation of the compositions and/or the hydrolyzing of the silanes, the compositions such as concentrates and baths and their properties, the effects, the formation of the coatings such as the drying, filming and curing, for example, the compositions and the properties of the coatings formed, and also the variants of the processes.

WO 01/90267 A2 relates to compositions which comprise a fluorocarbon silane of specific composition, a surfactant, a polymerizable organosilane or a

polymerizable silicate, and a catalyst. This document does not mention any addition of organic polymer/copolymer.

WO 02/31062 A2 describes emulsions which comprise a fluorocarbon silane, a surfactant, and a silane selected from aminosilanes, epoxysilanes and mercaptosilanes, and optionally a "film-forming assistant" based on SiO_2, TiO_2, ZrO_2, organoalkoxysilane and/or polysilazane. This document does not mention any addition of organic polymer/copolymer either.

US 2001/0031811 A1 teaches coating compositions substantially consisting of (a) a total of 20-70% of two different silane monomers, (b) 1-60% of tetraalkoxysilane, (c) water-soluble organic polymer, (d) nonionic surfactant, (e) lower aliphatic alcohol, (f) catalytically acting water-soluble acid, and (g) water. A fluorosilane as well can additionally be added if required. Anti-reflective coatings and photochromic articles such as lenses are to be produced using these compositions.

It is an object of the invention to overcome the drawbacks of the prior art and in particular to propose a process for coating metallic surfaces which is suitable for coating parts and for coating metallic strips at high coating speeds, which can be employed substantially or entirely free from chromium(VI) compounds, and which is extremely easy to employ industrially.

It has surprisingly been found that the addition even of a comparatively small amount of a fluorine-containing silane to an aqueous composition allows coatings to be produced which are much more hydrophobic

and corrosion-resistant than comparable coatings without the addition of fluorine-containing silane, without thereby substantially impairing the water-solubility of the composition or its stability. Normally the expectation would be that the more hydrophobic composition would also lead to a distinct deterioration in water-solubility.

The object is achieved with a process for coating a metallic surface, in particular of aluminum, iron, copper, magnesium, nickel, titanium, tin, zinc or alloys containing aluminum, iron, copper, magnesium, nickel, titanium, tin and/or zinc, with an aqueous composition, also comprising, if desired, organic solvent and other components, which is substantially or entirely free from chromium(VI) compounds, for the purpose of pretreatment prior to a further coating or for treatment where the article to be coated - in particular a strip or strip section - is, if desired, formed after coating, which process is characterized in that the composition comprises, besides water,

a) at least one hydrolyzable and/or at least partly hydrolyzed fluorine-free silane and

b) at least one hydrolyzable and/or at least partly hydrolyzed fluorine-containing silane, and

c) at least one metal chelate or/and

d) at least one oligomer/polymer/copolymer,

the ratio of the monomers/oligomers/polymers/co-polymers of component d) to silanes (a) and b)) in the

concentrate and/or in the bath being in the range from 0.1:1 to 10:1,

the silanes in the composition being water-soluble or becoming water-soluble in particular by virtue of (further) hydrolysis reactions and/or chemical reactions prior to application to the metallic surface,

the clean, pickled, cleaned and/or pretreated metallic surface being contacted with the aqueous composition and a film being formed on the metallic surface and subsequently dried and, if desired, additionally cured,

the dried and, where appropriate, also cured film having a thickness in the range from 0.001 to 10 µm, determined by detaching a defined area of the cured film and weighing it or by determining the silicon content of the coating, for example with X-ray fluorescence analysis and corresponding conversion.

The object is also achieved by aqueous compositions corresponding to claim 25.

The dependent claims develop the process further. Uses can be found in claim 26 and claim 27.

The silane is characterized in this specification by the dominant constituent of the products, which are generally available commercially. The silanes present in the aqueous composition (concentrate or bath) are monomers, oligomers, polymers, copolymers and/or reaction products with further components as a result of hydrolysis reactions, condensation reactions and/or further reactions. The reactions take place primarily in solution, in the course of the drying and, where appropriate, curing of the coating. The term "silane"

is utilized in this context for silanes, silanols, siloxanes, polysiloxanes and their reaction products and/or derivatives, which are often "silane" mixtures. In view of the often highly complex chemical reactions which occur in this context, and in view of highly complex analyses and operations,

Claims

1. A process for coating a metallic surface, with an aqueous composition, also comprising, if desired, organic solvent and other components, which is substantially or entirely free from chromium(VI) compounds, for the purpose of pretreatment prior to a further coating or for treatment, which process is characterized in that the composition comprises, besides water,

   a) at least one hydrolyzable and/or at least partly hydrolyzed fluorine-free silane and

   b) at least one hydrolyzable and/or at least partly hydrolyzed fluorine-containing silane, and

   c) at least one metal chelate or/and

   d) at least one oligomer/polymer/copolymer,

   the ratio of the monomers/oligomers/polymers/copolymers of component d) to silanes (a) and b)) in the concentrate and/or in the bath being in the range from 0.1:1 to 10:1,

   the silanes in the composition being water-soluble or becoming water-soluble in particular by virtue of (further) hydrolysis reactions and/or chemical reactions prior to application to the metallic surface,

   the clean, pickled, cleaned and/or pretreated metallic surface being contacted with the aqueous composition and a film being formed on the

metallic surface and subsequently dried and, if desired, additionally cured,

the dried and, where appropriate, also cured film having a thickness in the range from 0.001 to 10 µm.

2. Process according to claim 1, characterized in that in the aqueous composition selected from the fluorine-free silanes there is in each case at least one acyloxysilane, alkoxysilane, silane having at least one amino group such as an aminoalkylsilane, silane having at least one succinic group and/or succinic anhydride group, bis-silyl-silane, silane having at least one epoxy group such as a glycidyloxysilane, (meth)acrylato-silane, multi-silyl-silane, ureidosilane, vinylsilane and/or at least one silanol and/or at least one siloxane or siloxane whose composition corresponds chemically to that of the aforementioned silanes.

3. Process according to claim 1 or 2, characterized in that there is at least one fluorine-free silane selected from the group consisting of, or based on,

glycidyloxyalkyltrialkoxysilane,
methacryloyloxyalkyltrialkoxysilane,
(trialkoxysilyl)alkylsuccinoylsilane,
aminoalkylaminoalkylalkyldialkoxysilane,
(epoxycycloalkyl)alkyltrialkoxysilane,
bis(trialkoxysilylalkyl)amine,
bis(trialkoxysilyl)ethane,
(epoxyalkyl)trialkoxysilane,
aminoalkyltrialkoxysilane,
ureidoalkyltrialkoxysilane,

N-(trialkoxysilylalkyl)alkylenediamine,
N-(aminoalkyl)aminoalkyltrialkoxysilane,
N-(trialkoxysilylalkyl)dialkylenetriamine,
poly(aminoalkyl)alkyldialkoxysilane,
tris(trialkoxysilyl)alkyl) isocyanurate,
ureidoalkyltrialkoxysilane and
acetoxysilane.

4. Process according to one of the above claims, characterized in that there is at least one silane selected from the group consisting of, or based on,

3-glycidyloxypropyltriethoxysilane,
3-glycidyloxypropyltrimethoxysilane,
3-methacryloyloxypropyltriethoxysilane,
3-methacryloyloxypropyltrimethoxysilane,
3-(triethoxysilyl)propylsuccinoylsilane,
aminoethylaminopropylmethyldiethoxysilane,
aminoethylaminopropylmethyldimethoxysilane,
beta-(3,4-epoxycyclohexyl)ethyltriethoxysilane,
beta-(3,4-epoxycyclohexyl)ethyltrimethoxysilane,
beta-(3,4-epoxycyclohexyl)methyltriethoxysilane,
beta-(3,4-epoxycyclohexyl)methyltrimethoxysilane,
gamma-(3,4-epoxycyclohexyl)propyltriethoxysilane,
gamma-(3,4-epoxycyclohexyl)propyltrimethoxysilane,
bis(triethoxysilylpropyl)amine,
bis(trimethoxysilylpropyl)amine,
(3,4-epoxybutyl)triethoxysilane,
(3,4-epoxybutyl)trimethoxysilane,
gamma-aminopropyltriethoxysilane,
gamma-aminopropyltrimethoxysilane,
gamma-ureidopropyltrialkoxysilane,
N-(3-(trimethoxysilyl)propyl)ethylenediamine,
N-beta-(aminoethyl)-gamma-aminopropyltriethoxysilane,
N-beta-(aminoethyl)-gamma-aminopropyltrimethoxysilane,
N-(gamma-triethoxysilylpropyl)diethylenetriamine,

N-(gamma-trimethoxysilylpropyl)diethylenetriamine,
N-(gamma-triethoxysilylpropyl)dimethylenetriamine,
N-(gamma-trimethoxysilylpropyl)dimethylenetriamine,
poly(aminoalkyl)ethyldialkoxysilane,
poly(aminoalkyl)methyldialkoxysilane,
tris(3-(triethoxysilyl)propyl) isocyanurate,
tris(3-(trimethoxysilyl)propyl) isocyanurate and
vinyltriacetoxysilane.

5. Process according to one of the above claims, characterized in that in the aqueous composition selected from the fluorine-containing silanes there is in each case at least one acyloxysilane, alkoxysilane, alkoxysilane, silane having at least one amino group such as an aminoalkylsilane, silane having at least one succinic acid group and/or succinic anhydride group, bis-silyl-silane, silane having at least one epoxy group such as a glycidyloxysilane, (meth)acrylato-silane, multi-silyl-silane, ureidosilane, vinylsilane and/or at least one silanol and/or at least one siloxane or polysiloxane whose composition corresponds chemically to that of the aforementioned silanes, containing in each case at least one group that contains at least one fluorine atom.

6. Process according to one of claims 1 or 5, characterized in that the aqueous composition comprises at least one fluoroalkoxyalkylsilane, at least one mono-, di- or trifunctional fluorosilane, at least one mono-, bis- or tris-fluorosilane, at least one fluorosilane based on ethoxysilane and/or based on methoxysilane and/or at least one fluorosilane having at least one functional group such as, for example, an amino group, in particular in the form of a cocondensate, such as fluoroalkyldialkoxysilane,

a fluoroaminoalkylpropyltrialkoxysilane, a fluoromethanesulfonate, a fluoropropylalkyldialkoxysilane, a triphenylfluorosilane, a trialkoxyfluorosilane, a trialkylfluorosilane and/or a tridecafluorooctyltrialkoxysilane.

7. Process according to one of claims 1, 5 or 6, characterized in that the silane contains at least two amino groups and also at least one ethyl group and/or at least one methyl group.

8. Process according to one of the above claims, characterized in that in the aqueous composition there is also at least one component e) selected from the group consisting of:

e_1) at least one inorganic compound in particle form, having an average particle diameter, measured on a scanning electron microscope, in the range from 0.005 to 0.3 µm in diameter,

e_2) at least one lubricant,

e_3) at least one organic corrosion inhibitor,

e_4) at least one anti-corrosion pigment,

e_5) at least one agent for neutralizing and/or sterically stabilizing the synthetic resins,

e_6) at least one organic solvent,

e_7) at least one siloxane,

e_8) at least one long-chain alcohol, and

e_9) at least one surfactant.

9. Process according to one of the above claims, characterized in that the organic film former is a synthetic resin mixture of at least one polymer and/or at least one copolymer, comprising synthetic resin based on acrylate, epoxide, ethylene, urea-formaldehyde, phenol, polyester, polyurethane, styrene, styrene-butadiene and/or vinyl.

10. Process according to one of the above claims, characterized in that the organic film former also comprises as synthetic resin an amount of organic polymer, copolymer and/or mixtures thereof based on polyethyleneimine, polyvinyl alcohol, polyvinylphenol, polyvinylpyrrolidone and/or polyaspartic acid, in particular copolymers with a phosphorus-containing vinyl compound.

11. Process according to one of the above claims, characterized in that the acid groups of the synthetic resins are stabilized with ammonia, with amines such as morpholine, dimethylethanolamine, diethylethanolamine or triethanolamine and/or with alkali metal compounds such as sodium hydroxide.

12. Process according to one of the above claims, characterized in that the aqueous composition contains from 0.1 to 980 g/l of the organic film former, preferably from 2 to 600 g/l.

13. Process according to one of the above claims, characterized in that the amount of at least one fluorine-free silane in the aqueous composition, including the reaction products formed therefrom, is preferably from 0.05 to 300 g/l.

14. Process according to one of the above claims, characterized in that the amount of at least one fluorine-containing silane in the aqueous composition, including the reaction products formed therefrom, is preferably from 0.01 to 150 g/l.

15. Process according to one of the above claims, characterized in that the at least one metal

chelate is selected from chelate complexes based on acetylacetonates, acetoacetic esters, acetonates, alkylenediamines, amines, lactates, carboxylic acids, citrates and/or glycols, the amount of at least one chelate in the aqueous composition, including any reaction products formed therefrom, being preferably from 0.1 to 80 g/l.

16. Process according to one of the above claims, characterized in that as inorganic compound in particle form a finely divided powder, a dispersion or a suspension such as a carbonate, oxide, silicate or sulfate is added, especially colloidal and/or amorphous particles.

17. Process according to one of the above claims, characterized in that as inorganic compound in particle form particles are added based on at least one compound of aluminum, of barium, of cerium, of calcium, of lanthanum, of silicon, of titanium, of yttrium, of zinc and/or of zirconium.

18. Process according to one of the above claims, characterized in that as lubricant at least one wax is used selected from the group consisting of paraffins, polyethylenes and polypropylenes, in particular an oxidized wax, the amount of waxes in the aqueous composition being preferably in the range from 0.01 to 5% by weight.

19. Process according to one of the above claims, characterized in that the coating is partly produced by drying and filming and/or is cured by actinic radiation, cationic polymerization and/or thermal crosslinking.

20. Process according to one of the above claims, characterized in that the aqueous composition comprises at least one additive, in particular at least one selected from the group consisting of at least one biocide, at least one defoamer and/or at least one wetting agent.

21. Process according to one of the above claims, characterized in that the coated metallic surface is dried at a temperature in the range from 20 to 400°C forced-air temperature.

22. Process according to one of the above claims, characterized in that the aqueous composition is applied by rolling, flow coating, knife coating, spraying, squirting, brushing or dipping and if desired by subsequent squeezing off with a roller.

23. Process according to one of the above claims, characterized in that in each case at least one coating of printing ink, film, paint, paint-like material, powder coating material, adhesive and/or adhesive backing is applied to the dry and also, where appropriate, cured film.

24. Process according to one of the above claims, characterized in that the coated metal parts, strips or strip sections are formed, painted, coated with polymers such as PVC, for example, printed, bonded, hot-soldered, welded and/or joined with one another or with other elements by clinching or other joining techniques.

25. An aqueous composition for pretreating a metallic surface prior to a further coating or for treating the said surface, characterized in that the composition comprises, besides water,

a) at least one hydrolyzable and/or at least partly hydrolyzed fluorine-free silane and

b) at least one hydrolyzable and/or at least partly hydrolyzed fluorine-containing silane, and

c) at least one metal chelate or/and

d) at least one oligomer/polymer/copolymer,

the ratio of the monomers/oligomers/polymers/co-polymers of component d) to silanes (a) and b)) in the concentrate and/or in the bath being in the range from 0.1:1 to 10:1,

the proportion of a) to b) in each case including the reaction products formed therefrom being preferably in the range from 1:0.01 to 1:4 and

the silanes in the composition being water-soluble or in particular water-soluble owing to (further) hydrolysis reactions and/or chemical reactions.

26. The use of the substrates coated by the process as claimed in at least one of claims 1 to 25 above as wire, strip, sheet or part for a wire winding, a wire mesh, a steel strip, a metal sheet, a panel, a shield, a vehicle body or part of a vehicle body, a part of a vehicle, trailer, mobile home or missile, a cover, a casing, a lamp, a light, a traffic light element, a furniture item or furniture element, an element of a household appliance, a frame, a profile, a molding of complex geometry, a guideboard element, radiator element or fencing element, a fender, a part of or

with at least one pipe and/or profile, a window frame, door frame or cycle frame or a small part such as a bolt, nut, flange, spring or a spectacle frame.

27. The use of the composition according to one of claims 1 to 25 as an afterrinse solution, which is applied to a preceding coating such as, for example, to a conversion coating, and/or as a composition for blank corrosion protection.